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(72) Inventor: **Bramley, Christopher Sinjin**
Tyne & Wear NE8 1RU (GB)

(74) Representative: **Kirkham, Nicholas Andrew et al**
Graham Watt & Co.
St. Botolph's House
7-9 St. Botolph's Road
Sevenoaks Kent TN13 3AJ (GB)

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(71) Applicant: **Akzo Nobel Decorative Coatings Ltd.**
Darwen, Lancashire BB3 0BG (GB)

(54) **Colour changing paint**

(57) A composition comprising a paint and a secondary dye, the dye colourant being a first colour when in a liquid phase with the paint and a second colour when in a dried phase with the paint.

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Description

[0001] The present invention relates to a composition comprising a paint and a method of painting a wall.

[0002] Paints can, of course, be applied to a wide variety of different surfaces such as metal, plaster based walls, plastics, etc. The methods for making suitable paints are well known to those skilled in the art. The present invention is applicable to all types of paint products but in particular to emulsion or aqueous-based wall paints.

[0003] When painting a surface it is sometimes important to know whether or not an even and full coat of paint has been applied to a particular area. For example, when applying a second coat to a wall it is often difficult to tell whether or not the second coat has been evenly applied until after the paint dries. This would be particularly useful to a person with visual impairment when painting. This then leads to additional coats being necessary which is wasteful in terms of time and the amount of paint required.

[0004] The present invention seeks to provide a composition comprising a paint.

[0005] According to a first aspect the present invention there is provided a composition comprising a paint and a secondary dye, the secondary dye being a first colour in a liquid phase with the paint and a second colour in a dry phase with the paint. The addition of the secondary dye into the paint composition allows for obvious visual examination on whether or not a paint coat is being evenly applied even as a top coat over a lower coat which is of the same colour as the dried composition. When the secondary dye changes to another colour in the dried phase, the composition will then be in a finished colour which of course would have to be the desired paint colour.

[0006] The secondary dye will often be substantially colourless or white when in said dried phase, thus allowing the paint to provide the finished colour.

[0007] The secondary dye will normally be an additive to a base paint which base paint can be prepared by normal methods. Alternatively, the basic paint could be modified such that one of the components of the base paint becomes the secondary dye and this modified component loses its colour as the paint dries. For example, that part of the alkyl monomer dispersed in the paint is coloured and becomes transparent upon polymerisation.

[0008] The present invention thus provides a definite cost saving especially in commercial/decoration field. Even if the top coat paint were retailed at a higher price than a conventional paint, the saving in time and material would be demonstrable and not need re-rollering or touching-up.

[0009] In a further embodiment, the invention provides a composition wherein the secondary dye reacts with a component of air, e.g. oxygen or CO₂, to form said second colour.

[0010] In another embodiment, the invention provides a composition wherein additionally or alternatively the secondary dye is an ionic species with the ion forming said first colour in said liquid phase.

[0011] The choice of the additive is, and the chemistry of the colour change is principally constrained by the skilled persons preference and experience. However, the present inventor suggests that indicators, may provide one suitable solution.

[0012] Indicator chemistry is well known, for example see Acid-Base Indicators Kolthoff (Macmillan, New York 1937); Kolthoff and Stinger in Volumetric Analysis Vols I and II (Interscience, New York, 2nd Edition, 1942); Bates, Determination of pH (Wiley & Sons, New York, 1954); Bishop, Indicators (Pergamon Press, Oxford, 1972); Green, The Sigma-Aldrich Handbook of Stains, Dyes and Indicators (Aldrich, Milwaukee, Wisconsin, 1990). The choice of secondary dye will also be influenced on the nature of the paint as of course it must not undermine the normal paint finish and qualities. For example, with indicators it may well be necessary to use a secondary additive such as a base e.g. NaOH or an acid in order to cause the necessary colour change.

[0013] The preferred indicators are shown in Table 1. The most preferred indicators are those in one of the states the indicator is non-coloured indicated in Table 1 as either the acid colour or the basic colour being C.

[0014] Other possible secondary dyes are photo-unstable compounds such that the colour is lost on exposure to light. In some instances this may not be preferred due to loss of colour too quickly in very bright conditions or too slowly when light conditions are poor.

[0015] In some circumstances, however this will be preferred. This will be particularly preferred where the compound is a photo-sensitive dye that fades on exposure to a specific frequency of electro-magnetic radiation e.g. UV or infrared. This would allow intimate and leisurely inspection of the top coat. The surface would then be illuminated with the specific frequency of electro-magnetic radiation once the coating had been fully inspected and passed as fit. The coating with the secondary dye would then be changed to the second colour allowing the composition to have its finished colour. This may be particularly suitable to instances of coating e.g. specialised pipes or the like.

[0016] The invention may be provided as an additive and sold separately from a normal paint. The additive would then be added by the consumer if desired for their particular purpose. In these instances it will be important that the paint is compatible with the particular secondary dye, and vice versa.

[0017] In some instances clearly a further agent such as clearing additive could be causing the secondary dye to slowly lose its colour from addition of the clearing additive. Alternatively, the clearing additive could be painted onto the dried paint causing a chemical reaction with the secondary dye and loss of colour. However, this is not a preferred

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method, but it may be useful where a sealing coat or lacquer is applied to the paint surface.

[0018] According to a second aspect of the invention there is provided a method of painting a surface comprising the steps of:

- 5 a) applying a liquid composition to the surface; and
 b) allowing the liquid composition to dry on said surface.

[0019] Other uses of the invention would be to provide a photo-sensitive paint that could be used for providing striped or other pattern on the wall and then changed colour when the paint dried. Alternatively, a photo-sensitive paint could be used and an image projected on to it to cause the changing of the fixative agent in particular areas.

[0020] Preferred embodiments of the present invention will now be described.

Example 1

15 [0021] Phenolphthalein solution at pH 9.5 is a red colour but if the solution is dried only white crystals remain. A phenolphthalein solution was thus mixed with white paint Wilkonson Wilko-brand vinyl silk emulsion (Brilliant White) which had been made basic by the addition of NaOH solution. Phenolphthalein was added in an amount of about 0.05% by weight. When added this turned the white paint a bright pink when applied to the wall but when dried is a brilliant white.

20 Example 2

[0022] The same composition was made as Example 1 except that the secondary dye was changed to thymolphthalein. This shows a bright blue colour when mixed in the liquid phase with the paint and fades to transparent when dry under similar conditions. Thus providing a brilliant finish is the dried phase in brilliant white paint.

25 [0023] Alternatively ammonia or other basic compounds could be used to provide the basic agent. This evaporates rather more quickly from the paint and causes the loss of colour while the paint is still wet. However, in commercial applications it is not imagined that ammonium will provide a suitable secondary additive.

[0024] It is preferred if no additional additive has to be used. Thus an indicator or other dye which undergoes colour changes in the normal pH of the paint will often be preferred. For example, quinoline blue changes at pH 7.0-8.0 which is the normal pH of many household emulsion paints. Thus no base would be required.

Indicators

35 [0025] The following tables list indicators commonly used in acid-base titrimetry for visible end-point determinations. Table 1 lists individual compounds which exhibit a color change over a range of pH values. Table 2 lists mixtures of compounds which exhibit a very sharp color change at a specific pH.

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Table 1

Indicator	Chemical name	Acid color ¹	pH range	Basic color ¹	Preparation of stock solution
methyl violet	mixture of tetra-, penta-, and hexamethyl- <i>p</i> -rosaniline hydrochloride salts	Y	0.15-3.2	Y	0.01-0.06% in water
cresol red (acid range)	<i>o</i> -cresolsulfonaphthalein	R	0.2-1.8	Y	Dissolve 100 mg in 2.65ml 0.1 <i>N</i> NaOH, dil to 100 ml with water
metanil yellow	4'-aminoazobenzene- <i>m</i> -sulfonic acid, sodium salt	R	1.2-2.3	Y	0.01-0.1% in water
<i>m</i> -cresol purple (acid range)	<i>m</i> -cresolsulfonaphthalein	R	1.2-2.8	Y	Dissolve 100 mg in 2.65 ml 0.1 <i>N</i> NaOH, dil to 100ml with water
xylenol blue (acid range)	<i>p</i> -xylenolsulfonaphthalein	R	1.2-2.8	Y	Dissolve 40 mg in 0.98 ml 0.1 <i>N</i> NaOH, dil to 100ml with water
thymol blue (acid range)	thymolsulfonaphthalein	R	1.2-2.8	Y	Dissolve 100 mg in 2.15 ml 0.1 <i>N</i> NaOH, dil to 100ml with water
tropaeolin OO	4'-phenylaminoazobenzene-4-sulfonic acid, sodium salt	R	1.3-3.2	Y	1% in water, 0.4% in 50% aq alc ³
quinadine red	2-(<i>p</i> -dimethylaminostyryl)-quinoline ethiodide	C	1.4-3.2	R	0.1% in alc or 80% aq ethanol ³
α -dinitrophenol	2,4 dinitrophenol	C	2.0-4.7	Y	0.1% in 70% aq alc ³
methyl yellow; dimethyl yellow	<i>p</i> -dimethylaminoazobenzene	R	2.8-4.0	Y	0.1% in 90% aq alc ³
bromophenol blue	3,3',5,5'-tetrabromophenolsulfonaphthalein	Y	3.0-4.6	Pu	Dissolve 100mg in 1.5ml 0.1 <i>N</i> NaOH, dil to 100ml with water

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Table 1 (continued)

Indicator	Chemical name	Acid color ¹	pH range	Basic color ¹	Preparation of stock solution
tetrabromophenol blue	tetrabromophenol tetrabromosulfonephthalein	Y	3.0-4.6	B	Dissolve 100mg in 1.01ml-0.1N NaOH, dil to 100ml with water
bromochlorophenol blue	3,3'-dibromo-5,5'- dichlorophenolsulfonephthalein	Y	3.0-4.6	Pu	Dissolve 40mg in 0.69 ml 0.1M NaOH, dil to 100ml with water
Congo red	diphenyl-4,4'-bis-(2-azo- 1-naphthylamine)sulfonic acid, sodium salt	B	3.0-5.2	R	0.1% in water
methyl orange	4'-dimethylaminoazobenzene-4-sulfonic acid, sodium, salt	R	3.1-4.4	O	0.04-0.1% in water
p-ethoxychrysoidine hydrochloride	4-ethoxy-2',4'-diaminoazobenzene hydrochloride	R	3.6-6.5	Y	0.1% in 90% aq alc ³ ; 0.2% in alc
naphthyl red	α -naphthylaminoazobenzene	R	3.7-5.0	Y	0.1% in ethanol or 70% aq alc ³
alizarin sodium sulfonate	dihydroxyanthraquinone sodium sulfonate	Y	3.7-5.2	V	0.1% in water
bromocresol green	3,3',5,5'-tetrabromo- <i>m</i> - cresolsulfonephthalein	Y	3.8-5.4	B	Dissolve 100mg in 1.45 ml 0.1N NaOH, dil to 100ml with water
γ -dinitrophenol	2,5-dinitrophenol	C	4.0-5.8	Y	0.1% in 70% aq alc ³
methyl red	4'-dimethylaminoazobenzene- 2-carboxylic acid	R	4.4-6.2	Y	Dissolve 100mg in 3.7ml 0.1N NaOH, dil to 100ml with water, .1% in alc
lacmoid		R	4.4-6.4	B	0.2% in alc

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Table 1 (continued)

Indicator	Chemical name	Acid color ¹	pH range	Basic color ¹	Preparation of stock solution
chlorophenol red	3,3'-dichlorophenolsulfonaphthalein	Y	4.8-6.4	Pu	Dissolve 100mg in 235 ml 0.1N NaOH, dil to 100ml with water
benzoyl auramine G		V	5-5.6	Y	0.25% in methanol
bromocresol purple	5,5'-dibromo-o-cresolsulfonaphthalein	Y	5.2-6.8	Pu	Dissolve 100mg in 1.85 ml 0.1N NaOH, dil to 100ml with water
bromophenol red	3,3'-dibromophenolsulfonaphthalein	Y	5.2-6.8		Dissolve 40mg in 0.78ml 0.1N NaOH, dil to 100ml with water
bromophenol red	3,3'-dibromophenolsulfonaphthalein	Y	5.2-6.8	R	Dissolve 40 mg in 0.78 ml 0.1N NaOH, dil to 100ml with water
p-nitrophenol		C	5.6-7.5	Y	0.1% in water; 0.2% in alc
bromothymol blue	3,3'-dibromothymolsulfonaphthalein	Y	6.0-7.6	B	Dissolve 100mg in 1.8 ml 0.1N NaOH, dil to 100ml with water
phenol red	phenolsulfonaphthalein	Y	6.4-8.2	R	Dissolve 100mg in 2.85 ml 0.1N NaOH, dil to 100ml with water
rosolic acid; aurin	p-quinonemono(bis-4-oxyphenylmethide)	Y	6.6-8.0	R	0.2% in 50% aq alc ³
neutral red	3-amino-6-dimethylamino-2-methylphenazinium chloride	R	6.8-8.0	Y	0.1% in 70% aq alc ³
quinoline blue		C	7.0-8.0	V	1% in alc
cresol red (basic range)	o-cresolsulfonaphthalein	Y	7.0-8.8	R	Dissolve 100 mg in 2.85 ml 0.1N NaOH, dil to 100ml with water

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Table 1 (continued)

Indicator	Chemical name	Acid color ¹	pH range	Basic color ¹	Preparation of stock solution
α -naphtholphthalein		C	7.3-8.7	G-B	0.1% in alc or 70% eq alc ³
tropaeolin OOO; α -naphthol orange	α -naphtholazobenzene- <i>p</i> -sulfonic acid, sodium salt	Y	7.4-8.9	P	0.1% in water
η -cresol purple (basic range)	<i>m</i> -cresolsulfonephthalein	Y	7.4-9.0	Pu	Dissolve 100 mg in 2.65 ml 0.1N NaOH, dil to 100ml with water
ethyl bis(2,4-dinitrophenyl)acetate					
thymol blue (basic range)	thymolsulfonephthalein	C	7.5-8.1	B	said soln in 1:1 acetone-alc
xylenol blue (basic range)	<i>p</i> -xylenolsulfonephthalein	Y	8.0-9.8	B	Dissolve 100mg in 2.15 ml 0.1N NaOH, dil to 100ml with water
<i>o</i> -cresolphthalein	<i>o</i> -cresolphthalein	Y	8.0-9.8	B	Dissolve 40mg in 0.98 ml 0.1M NaOH, dil to 100ml water
phenolphthalein	di- <i>o</i> -cresolphthaleide	C	8.2-9.8	R-V	0.04% in 50% eq alc ³
thymolphthalein	di- <i>p</i> -dioxycidphenylphthalide	C	8.2-8.8	P	0.1% in alc or 60% eq alc ³
α -naphtholbenzein	dithymolphthalide	C	9.3-10.5	B	0.1% in 80% eq alc ³
alizarin yellow GG; salicyl yellow	dimethylphenolphthalein	Br	9.8-11.0	G-B	0.1% in alc
alizarin yellow R	3'-nitro-4-oxyazobenzene-3-carboxylic acid, sodium salt	Y	10.0-12.1	Br-Y	0.1% in ethanol or water
Nile blue	4'-nitro-4-oxyazobenzene-3-carboxylic acid, sodium salt	Y	10.0-12.1	R	0.1% in water
	diethylaminonaphthophenoxonium sulfate	B	10.1-11.1	R	0.1 % in water

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Table 1 (continued)

Indicator	Chemical name	Acid color ¹	pH range	Basic color ¹	Preparation of stock solution
nitramine	2,4,6-trinitrophenylmethylnitramine	C	10.8-13.0	Br	0.1% in 70% aq alc ³
tropaeolin O	2',4'-dioxazobenzene-4-sulfonic acid, sodium salt	Y	11.0-12.7	R-Br	0.1% in water
Poirrier blue C4B	triphenylrosaniline sulfonic acid, sodium or potassium salt	B	11.0-13.0	Pu	0.1% in water
indigo carmine	indigo(1n-5,5'-disulfonic acid, disodium salt	B	11.5-14.0	Y	0.25% in 50% aq ethanol ³
trinitrobenzene		C	12.0-14.0	O	0.1% in 70% aq alc ³

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Table 2

	Composition of indicator stock solution ²	Solvent	Acid color ¹	Transition pH	Basic color ¹
5	dimethyl yellow, 0.05% + methylene blue, 0.05%	alc	B-V	3.25	G
	methyl orange, 0.1% + indigo carmine, 0.25%	aq	V	4.1	G
10	bromocresol green, sodium salt, 0.05% + methyl orange, 0.01%	aq	O	4.3	B-G
	bromocresol green, 0.075% + methyl red, 0.05%	alc	wine-R	5.1	G
15	methyl red, 0.1% + methylene blue, 0.05%	alc	R-V	5.4	G
	bromocresol green, sodium salt, 0.05% + chlorophenol red, sodium salt, 0.05%	aq	Y-G	6.1	B-V
20	bromocresol purple, sodium salt, 0.05% + bromothymol blue, sodium salt, 0.05%	aq	Y	6.7	V-B
	neutral red, 0.05% + methylene blue, 0.05%	alc	V-B	7.0	G
25	bromothymol blue, sodium salt, 0.05% + phenol red, sodium salt, 0.05%	aq	Y	7.5	V
	cresol red, sodium salt, 0.025% + thymol blue, sodium salt, 0.075%	aq	Y	8.3	V
30	phenolphthalein, 0.075% + α -naphtholphthalein, 0.025%	alc	P	8.9	V
	phenolphthalein, 0.075% + thymol blue, 0.025%	50% alc	Y	9.0	V
35	phenolphthalein, 0.05% + thymolphthalein, 0.05%	alc	C	9.9	V
	phenolphthalein, 0.033% + Nile blue, 0.133%	alc	B	10.0	R

¹The indicator colors are abbreviated as follows: B - blue; Br - brown; C - colorless; G - green; O - orange; P - pink; Pu - purple; R - red; V - violet; and Y - yellow.

²One to five drops of the indicator stock soln should be added to every 10ml soln to be titrated.

³When preparing the aq alc solns, it is important to dissolve the indicator in alc first and then dil with water to the indicated conc. For example, to make a 0.1% soln in 70% aq alc, dissolve 100mg indicator in 70ml alc, then add 30ml water.

References

[0026]

I M. Kolthoff, *Acid-Base Indicators* (Macmillan, New York, 1937).

I M. Kolthoff, V. A. Stenger, *Volumetric Analysis* vols. I, II (Interscience, New York, 2nd ed., 1942).

R G. Bates, *Determination of pH* (Wiley & Sons, New York, 1954).

E. Bishop, *Indicators* (Pergamon Press, Oxford, 1972).

F. J. Green, *The Sigma-Aldrich Handbook of Stains, Dyes, and Indicators* (Aldrich, Milwaukee, Wisconsin, 1990).

Claims

1. A composition comprising a paint and a secondary dye, the secondary dye being a first colour when in a liquid phase with the paint and a second colour when in a dried phase with the paint.

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2. The composition according to claim 1, wherein the secondary dye:

- (a) is substantially colourless or white in said dried phase; and/or
(b) reacts with a component of air, e.g. oxygen or CO₂, to form said second colour; and/or
(c) is an ionic species with the ion forming said first colour in said liquid phase; and/or
(d) is an indicator.

3. The composition according to any one of the preceding claims, further including an additive selected to interact with the secondary dye to form the first colour; and optionally wherein the additive is selected from the group consisting of: bases, acids and buffers.

4. The composition according to claim 2, wherein the indicator:

- (a) exists as either a protonated or an unprotonated form, only one of which form is coloured; and/or
(b) is selected from the indicators shown in Table 1; and/or
(c) is selected from the groups consisting of quinaldine red, α -dinitrophenol γ -dinitrophenol, p-nitrophenol, quinoline blue, α -naphtholphthalein, ethyl bis(2,4-dinitro-phenyl)acetate, α -cresolphthalein, phenolphthalein, thymolphthalein, nitramine and trinitrobenzene.

5. The composition according to any one of the preceding claims, wherein the paint is an aqueous-based paint.

6. The composition according to any one of the preceding claims, wherein the secondary dye is substantially colourless when in said dried phase.

7. A method of painting a surface comprising the steps of:

- a) applying a liquid composition to the surface; and
b) allowing the liquid composition to dry on said surface;

wherein the composition comprises a composition according to any one of claims 1 to 6.

8. The method of claim 7, wherein the paint dries within 4 hours of the end of step (a).

9. The method of claim 7 or claim 8, wherein the surface is a wall or plaster-based surface.

10. Use of a dye component for forming said secondary dye in a composition according to any one of claims 1 to 7.

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EUROPEAN SEARCH REPORT

Application Number

EP 03 25 5205

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 549 145 A (ROHM & HAAS) 30 June 1993 (1993-06-30) * page 2, line 32-50 * * page 3, line 33-57 * * page 4, line 21-25; table 1.2 *	1-10	C09D7/00
X	EP 0 488 980 A (FINA RESEARCH) 3 June 1992 (1992-06-03) * page 2, line 4-7 * * page 2, line 40-57 * * page 3, line 4-10 *	1-7,10	
X	CH 464 415 A (EBNOETHER MARCEL DR ; FLEURY PIERRE (CH)) 31 October 1968 (1968-10-31) * column 1, line 1-40 * * claims 1-5; examples 3,4 *	1-4,7,10	
X	AU 49046 72 A (DURALEX PAINTS PTY LTD) 23 May 1974 (1974-05-23) * page 2, line 6-25 * * page 3, line 4 - page 4, line 2 * * page 4, line 11 - page 5, line 21 *	1-3,5-7,10	
X	US 3 960 759 A (MALLIS JAMES N) 1 June 1976 (1976-06-01) * abstract * * claims 1-4 *	1,2,4,7,10	
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 017 (C-324), 23 January 1986 (1986-01-23) & JP 60 170674 A (TOSHIBA KK), 4 September 1985 (1985-09-04) * abstract *	1-5,7,10	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 November 2003	Examiner Miller, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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19-11-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0549145	A	30-06-1993	AU 659516 B2	18-05-1995
			AU 2999392 A	24-06-1993
			CA 2085079 A1	21-06-1993
			CN 1077970 A	03-11-1993
			CZ 9203751 A3	14-07-1993
			EP 0549145 A1	30-06-1993
			FI 925770 A	21-06-1993
			HU 63448 A2	30-08-1993
			JP 5331389 A	14-12-1993
			NO 924839 A	21-06-1993
			NZ 245368 A	27-04-1995
			PL 297069 A1	06-09-1993
			SK 375192 A3	10-05-1995
			TR 27518 A	07-06-1995
			ZA 9209755 A	21-06-1993
EP 0488980	A	03-06-1992	EP 0488980 A1	03-06-1992
			AT 203262 T	15-08-2001
			DE 69132661 D1	23-08-2001
			DE 69132661 T2	29-11-2001
			DK 488980 T3	22-10-2001
			ES 2160571 T3	16-11-2001
CH 464415	A	31-10-1968	NONE	
AU 4904672	A	23-05-1974	NONE	
US 3960759	A	01-06-1976	NONE	
JP 60170674	A	04-09-1985	JP 1838068 C	11-04-1994
			JP 5049712 B	27-07-1993

EPO/03/01/001

For more details about this annex : see Official Journal of the European Patent Office, No. 12/02